Effect of Low-Spin Fe^{2+} on the Composition of the Lower Mantle[1]

EDWARD S. GAFFNEY[2] AND DON L. ANDERSON

Seismological Laboratory, California Institute of Technology
Pasadena, California 91109

The effects of low-spin Fe^{2+} in the earth's lower mantle are investigated in considerable detail. The existence of low-spin Fe^{2+} permits the formation of an extra phase, since Mg^{2+} and low-spin Fe^{2+} probably do not form solid solutions. The elastic behavior of phases containing low-spin iron is predicted from bulk modulus systematics and is compared with available shock wave data. It is likely that the high-pressure phases of several ferrous iron compounds involve low-spin Fe^{2+}. Iron will be spin-paired in the mantle below 1700 km and perhaps at higher levels as well. The observed density and bulk modulus in the lower mantle are inconsistent with any combination of phases in a pyrolite bulk composition but can be fit quite well by a model with all Fe^{2+} spin-paired below 650 km. The lower mantle is richer in FeO and SiO_2 than the upper mantle. The spin-pairing of Fe^{2+} provides an excellent mechanism for both iron and silicon enrichment in the lower mantle by partial melting. Thus spin-pairing in iron provides support for previous arguments for chemical inhomogeneity of the mantle and also provides a mechanism for generating the inhomogeneity. This removes the motivation for reducing FeO and SiO_2 in the mantle to supply Fe and Si for the core.

Iron is involved in a number of controversies about the properties of the earth's lower mantle. The amount of iron has been the subject of much discussion for several years [*Anderson*, 1968; *Anderson and Jordan*, 1970; *Anderson et al.*, 1971; *Ringwood*, 1970], and this discussion depends critically on the spin state of Fe^{2+} in the lower mantle. In addition, many of the physical properties of the lower mantle, such as thermal conductivity [*Clark*, 1957; *Strens*, 1969; *Burns*, 1970; *Gaffney*, 1973, referred to here as paper 1] and seismic parameters, will depend on the spin state of Fe^{2+}. In the present work we assess the possible effects of low-spin Fe^{2+} in the earth's lower mantle. The presence and behavior of low-spin Fe^{2+} in this region will depend critically on the transition metal nature of Fe^{2+}, that is, on crystal field effects. In order to predict crystal effects on minerals in the mantle, we must first know three things: (1) what minerals are likely to contain ferrous iron in the mantle, and what the spin states of that iron will be, (2) what the response of these minerals is to high pressures, and (3) the effects of compression on the parameters used to describe the crystal fields.

This paper is an attempt to assess these three factors within the scope of a purely ionic approximation. This approach has been used primarily because of its simplicity. There is little doubt, however, that silicates often deviate from ideal ionicity and that more sophisticated techniques will be required to completely resolve the problems raised here.

MINERALOGY OF Fe^{2+} IN THE LOWER MANTLE

The mineralogy of Fe^{2+} in the lower mantle depends on the behavior of three ions: high-spin Fe^{2+}, low-spin Fe^{2+}, and Mg^{2+}. These ions have radii of 0.77, 0.61, and 0.72 A, respectively [*Shannon and Prewitt*, 1969]. The low-spin Fe^{2+} radius is based both on sulfide crystal structure data and on plots of ionic radius versus electronic configuration. Fe^{2+}(l.s.) has not been observed in either oxides or fluorides, nor has any other low-spin divalent first-row transition metal ion been observed in pure oxides. *Strens* [1966, 1969] reported the existence of spin-pairing of Fe^{2+} in gillespite ($BaFeSi_4O_{10}$) at about 25 kbar, and more recent data have supported this interpretation in general [*Abu-Eid et al.* 1973]. However, low-spin configurations of certain trivalent first-row transition metals

[1] Contribution 2233, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California.

[2] Now at Systems, Science and Software, La Jolla, California 92037.

are known Shannon and Prewitt plot ionic radius versus number of $3d$ electrons for these ions and find a fairly smooth variation from d^0 to d^6 (Co^{3+}) and from d^0 to d^{10} for the low-spin compounds. The values for Fe^{2+}(l.s.) and Co^{2+} deduced from sulfides behave in a very similar manner, and this lends some credence to the values given. However, in view of the indirect method of estimating the radius of Fe^{2+}(l.s.), a fairly large error must be attached to it, perhaps about 0.03 A. According to the Goldschmidt radius criterion for solid solubility (less than 15% difference in ionic radii), we can expect that Mg^{2+} and Fe^{2+}(h.s.) will form solid solutions but that Mg^{2+} and Fe^{2+}(l.s.) will not. By applying the phase rule we should expect that if Fe^{2+} goes to a low-spin ground state in the lower mantle another phase may appear. This possibility of a separate phase for Fe^{2+} (l.s.) leads to several more phase changes in the lower mantle.

The Goldschmidt radius criterion is only a rule of thumb to which numerous exceptions can be cited. At high temperatures it is to be expected that a large variability of size of cations could be accommodated in a solid solution. However, pressure should act to decrease the range of ionic sizes that can be accommodated. The net result is that it is difficult to predict how the criterion should be modified for use in the lower mantle. It will be used here, as was stated above, with the caveat that solid solution between Fe^{2+}(l.s.) and Mg^{2+} cannot be ruled out unequivocally in the lower mantle.

The phases possible with Mg^{2+} and Fe^{2+}(h.s.) are taken to be those of *Ringwood* [1970], so that there are two phase changes that can occur in pyrolite below 700 km:

$$(Mg, Fe)_2SiO_4 \text{ (strontium plumbate)} \rightarrow (Mg, Fe)_2SiO_4 \text{ (calcium ferrite or potassium nickel fluoride)} \quad (a)$$

$$(Mg, Fe)SiO_3 \text{ (ilmenite)} \rightarrow (Mg, Fe)SiO_3 \text{ (perovskite)} \quad (b)$$

No denser phases have been proposed, but *Johnson* [1969] and *Whitcomb and Anderson* [1970] and others have detected evidence for at least five discontinuities in the lower mantle.

It has already been pointed out (paper 1) that Fe^{2+} should 'prefer,' in any such reactions, to spin-pair and to enter the six-coordinate site of a calcium ferrite structure such as $Mg^{VIII}(FeSi)^{VI}O_4$. We shall also be interested here in other possible reactions involving low-spin Fe^{2+}. Three reactions are likely:

$$(Mg, Fe)_2SiO_4 \text{ (strontium plumbate)} \rightarrow MgFe(\text{l.s.})SiO_4 \text{ (calcium ferrite)} + Mg_2SiO_4 \quad (c)$$

$$MgFeSiO_4 \text{ (calcium ferrite)} + MgSiO_3 \rightarrow FeSiO_3 \text{ (ilmenite)} + Mg_2SiO_4 \quad (d)$$

$$FeSiO_3 \text{ (ilmenite)} + Mg_2SiO_4 \rightarrow FeO(\text{l.s., rock salt}) + 2MgSiO_3 \quad (e)$$

The zero pressure density of these proposed minerals can be estimated by using the radius of low-spin Fe^{2+} and various density systematics. For FeO in the rock salt structure, the relation $a_0 = 2(r(Fe^{2+}, \text{l.s.}) + r(O^{2-}))$ is used where $r(O^{2-})$ is taken as 1.38 A, which predicts the correct a_0 for MgO. Then a_0 (FeO, l.s.) = 3.99 A, and $\rho_0 = 7.55$ gm/cm^3. Using this value for ρ_0 (FeO, l.s.), and the relation [*Ringwood*, 1970] that ρ_0 (ilmenite) is 3% less than that of the isochemical mixture of oxides, one finds $\rho_0(FeSiO_3) = 5.43$ gm/cm^3.

For the density of $MgFeSiO_4$ in the calcium ferrite structure, two systematic relations derived from unit cell volume-ionic radius systematics are used. The first is the relation between unit cell volume (four formula units) and the radius of the octahedral ion for nine compounds $M^{2+}X_2^{3+}O_4$ in the calcium ferrite structure. The six compounds with M = Ca define a straight line. If this line is projected to the arithmetic or geometric mean of $r(Si^{4+})^{VI}$ and $r(Fe^{2+}, \text{l.s.})^{VI}$ the probable unit cell volume of $Ca(FeSi)O_4$ is obtained. (*Reid et al.* [1967] have shown that for $NaM^{3+}X^{4+}O_4$ compounds, the distribution M and X in the octahedral sites are completely random, so we are justified in treating the sites as equivalent even though they are crystallographically distinct. They also point out that the observed interatomic distances are very nearly equal to those derived by taking the mean of the two radii.) Next, it is noted that for the MSc_2O_4 and MIn_2O_4 compounds the difference in unit cell volume for M = Ca and M = Sr is a constant (20 A^3). From this the inference can be drawn that substitution of the M^{2+} ion can be treated as a sim-

ple addition of a constant to the unit cell volume determined for MX_2O_4 for the same X. For $MgSc_2O_4$ this term is a 8-A/unit cell so the unit cell volume inferred for $MgFeSiO_4$ is 240 A^3 or 236 A^3 for the arithmetic or geometric mean radius, respectively. The mean (238 A^3) leads to a density of 4.76 gm/cm^3.

A different approach to the same data leads to a similar conclusion. The percentage difference between the density of the mixed isochemical oxides and the calcium ferrite structure depends on the radius of the eight-coordinated divalent ion. Although calcium ferrite structures are up to 8.6% denser than the oxides for large divalent ions, they are actually less dense for small ions such as Mg^{2+}. Using the value of 2.5% (from $MgSc_2O_4$) for $MgFeSiO_4$, we again get a density of 4.76 g/cm^3. (In the section on elastic properties, we shall also need the density of Fe^{VIII}(h.s.)Fe^{VI}(l.s.)SiO_4 in this structure. Noting that in garnets Mg^{VIII} and Fe^{VIII}(h.s.) are almost identical in size [*Novak and Gibbs*, 1971], we predict a density of 5.63 g/cm^3 for this phase. If, on the other hand, we assume it is 2.5% less dense than the oxides, the density is 5.55 g/cm^3; thus we use $\rho_0 = 5.6 \pm 0.05$ g/cm^3.)

Although the potassium nickel fluoride and perovskite structures of most compounds should be considerably denser than the corresponding oxides, this will not be true for the low-spin ferrous minerals, because the Fe^{2+} must remain in six-coordination in order for the crystal field splitting of the 3*d* electronic energy levels to be sufficient to maintain the low-spin ground state. If the Si^{4+} were to go to coordination greater than six, these structures might include low-spin iron, but that is unlikely to occur below several megabars pressure, at which pressure the present approximation will certainly not be valid.

Response of Low-Spin Ferrous Minerals to Pressure

Having determined the structure and uncompressed density of possible low-spin ferrous minerals in the mantle, we now turn our attention to the effect of pressure. Again we employ systematics where we have no experimental data.

We use a plot of compressibility against incompressibility molecular volume for compounds of the composition MO involving both zincite and rock salt structures (Figure 1). Ignoring for the moment the transition metal oxides (except MnO, where Mn^{2+} has five *d* electrons in a half-filled shell, so that there are no crystal field effects), we see that there is a good fit to a straight line for all mean atomic weights

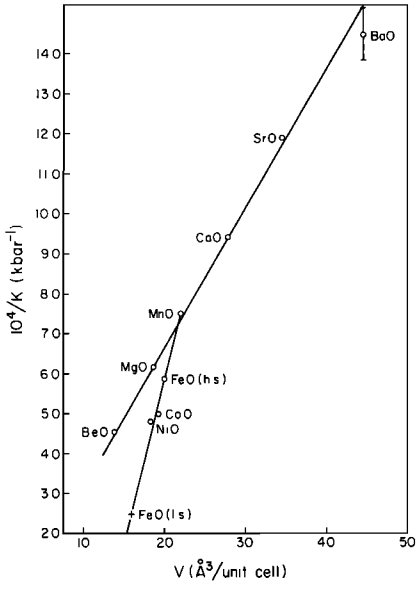

Fig. 1. Compressibility-density systematics for oxides MO.

$$\frac{1}{K\,(\mathrm{Mb})} = -0.04 + 0.035\,V_{\mathrm{molec}}\,(\mathrm{A}^3)$$

from which we would infer K(FeO,l.s.) = 1.950 Mbar. However, by considering the observed values for FeO, CoO, and NiO, we see that these compounds fall well below the curve. These cations have, respectively, one, two, and three *d* electrons contributing to crystal field effects. There seems, therefore, to be an effect due to these electrons leading to a different behavior. Indeed, the four transition metal oxides fall very close to a straight line themselves:

$$\frac{1}{K\,(\mathrm{Mb})} = -1.076 + 0.083\,V_{\mathrm{molec}}\,(\mathrm{A}^3)$$

Since Fe^{2+}(l.s.) also has *d* electrons contributing to crystal field effects (six of them), it seems preferable to use this relation to infer K(FeO, l.s.) = 4.160 Mb.

There are fewer data for sequioxides: the three oxides without crystal field effects (Al_2O_3, Fe_2O_3, and $SrTiO_3$) all lie on the line

$$\frac{1}{K\,(\mathrm{Mb})} = -0.04 + 0.01\,V_{\mathrm{molec}}\,(\mathrm{A}^3)$$

but the oxide Cr_2O_3 with two ions with crystal field effects lies slightly below that line. The Cr_2O_3 and Fe_2O_3 points are too close to justify the inference of a crystal field line as with MO; furthermore, the use of such a line derived for $M_2^{3+}O_3$ to predict behavior for $M^{2+}N^{4+}O_3$ crystal field effects would not appear, on the face of it, to be reasonable. Rather, we take Φ_0 for low spin FeO and assume that the Φ_0's of the oxides are additive in a compound whose density is near that of the mixture of oxides [*Anderson*, 1969]. Using $\Phi_0 = 82.2$ (km/sec)^2 for stishovite [*Mizutani et al.*, 1972], we find for $FeSiO_3$ and $MgFeSiO_4$ bulk moduli of 3.74 and 2.9 Mbar, respectively. (For Fe_2SiO_4 in the calcium ferrite structure, we get $K = 3.1 \pm 0.025$ Mbar.)

In order to estimate the magnitude of dK/dP in the high-pressure phases of the lower mantle, we have used a relation between the density and $(dK/dP - 5/3)$. In Figure 2 we show the experimental data taken from *Anderson et al.* [1968] and *Davies and Anderson* [1971]. Davies and Anderson's data are reduced from shock wave experiments and depend on the equation of state used by them. The values given by them for iron-rich compounds have been omitted for the present study. There is considerable scatter, but the points with mean atomic weight near 20 define a fairly good straight line on a log-log plot whose equation is

$$\frac{dK}{dP} = \frac{5}{3} + \left(\frac{k_{20}}{\rho}\right)^3$$

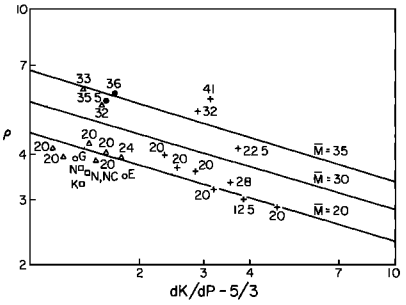

Fig. 2. Variation of dK/dP with density: plus sign, ultrasonic data [*Anderson et al.*, 1968]; solid circle, static compression data [*Clendenon and Drickamer*, 1966]; triangle, shock wave data [*Davies and Anderson*, 1971]; open circle, shock wave data for polymineralic rocks [*Davies and Anderson*, 1971] (*G*, granite; *E*, eclogite); square, shock wave data for feldspar-rich systems [*Davies and Anderson*, 1971] (N, albitite; K, microcline; N, NC, two points: oligoclase and anorthosite). Numbers by points are mean atomic weight $\langle M \rangle$.

where $k_{20} \sim 4.6$ cm^3/g. For greater mean atomic weights k_M is larger, about 5.6 for $\langle M \rangle = 30$ and 6.8 for $\langle M \rangle = 35$. We have used these relations with interpolation to infer dK/dP for mantle minerals. The properties of mantle minerals used in the paper are given in Table 1, along with the aggregate properties of some rocks composed of those minerals.

There is some experimental evidence supporting both the occurrence of low-spin iron at high pressures and the elastic properties we have predicted for such compounds. *McQueen et al.* [1967] have measured the Hugoniots of

TABLE 1. Properties of Mantle Minerals

Mineral Composition	Structure	ρ_0	$\langle M \rangle$	K_0, kb	Φ_0	K_0'
$(Mg_{0.89}Fe_{0.11})_2SiO_4$	Sr_2PbO_4	4.02	21.07	2302	57.26	3.17
	K_2NiF_4	4.17	21.07	2665	63.91	3.01
Mg_2SiO_4	Sr_2PbO_4	3.85	20.10	2272	59.00	3.37
	K_2NiF_4	3.99	20.10	2621	65.69	3.20
$Mg(FeSi)O_4$ (l.s.)	$CaFe_2O_4$	4.76	24.61	2900	60.92	2.69
$NaAlSiO_4$	$CaFe_2O_4$	3.90	20.29	2163	55.47	3.30
$(Mg_{0.89}Fe_{0.11})SiO_3$	Ilmenite	3.96	20.76	2280	59.57	3.23
	Perovskite	4.28	20.76	3111	72.69	2.91
$MgSiO_3$	Ilmenite	3.84	20.08	2255	58.72	3.39
	Perovskite	4.15	20.08	3076	74.12	3.02
$FeSiO_3$	Ilmenite	5.43	26.39	3740	68.88	2.45
$CaSiO_3$	Perovskite	3.97	23.23	3096	77.99	3.22
$Al_{1.64}Cr_{0.18}Fe_{0.18}O_3$	Sapphire	4.15	21.90	2032	48.95	3.02
FeO (low spin)	Rock salt	7.55	35.93	4160	55.10	2.40
Fe_2SiO_4	$CaFe_2O_4$	5.6	29.1	3100	55.36	2.65

TABLE 2. Properties of Mantle Mineral Assemblages

Rock	Composition	ρ_0	Φ_0	K_0	K_0'	ρ_{1600}	Φ_{1600}
A	0.36Ho + 0.64En (ilmenite)	4.21	59.5	2503	3.13	4.04	56.0
B	0.33Ho + 0.67Fo(str. plumb.)	4.13	60.6	2503	3.22	3.97	57.1
C	0.33Ho + 0.67Fo(K_2NiF_4)	4.25	64.0	2720	3.03	4.08	60.8
D	0.33Fs + 0.67Fo(K_2NiF_4)	4.35	66.5	2894	2.95	4.18	63.5
E	0.22Ho + 0.11Fs + 0.67En (perovskite)	4.46	70.5	3142	2.88	4.28	67.8
P1		4.00	58.5	2339	3.20	3.84	54.7
P2	*c*	4.03	60.0	2416	3.25	3.87	56.2
P3	*c, d*	4.05	61.1	2474	3.23	3.89	57.5
P4	*a, c*	4.08	62.1	2534	3.17	3.92	58.6
P5	*b, c, d*	4.12	65.1	2681	3.13	3.96	61.7
P6	*a, c, d*	4.13	66.2	2732	3.14	3.97	62.9
P7	*b, c*	4.13	62.9	2598	3.36	3.97	59.5
P8	*a, b, c*	4.19	64.1	2687	3.08	4.02	60.8
P9	*a, b, c, d*	4.20	68.2	2864	3.05	4.03	65.1
P10	*a, b, c, d, e*	4.24	69.3	2938	3.00	4.07	66.3

Ho, $MgFeSiO_4$(calc. ferr.); En, $MgSiO_3$; Fo, Mg_2SiO_4; Fs, $FeSiO_3$(ilmenite). For rocks P1 to P10, composition is that of pyrolite. *a, b, c, d,* and *e* indicate that those reactions have occurred. *a* and *b* refer to any composition of M_2SiO_4 and $MSiO_3$, respectively.

four iron-rich oxides: hortonolite dunite, fayalite, hematite, and magnetite (hortonolite dunite is a nearly monomineralic rock of approximate composition 90% olivine (fa_{65}), 97% bowlingite (alteration product of olivine), and 1% opaque minerals). G. F. Davies and Gaffney (in preparation, 1973) calculate the Hugoniots shown in Figure 3 from the elastic properties derived here, assuming that (1) hortonolite dunite and fayalite have both Fe^{2+}(l.s.) and Si^{4+} in six-coordination [and either Mg^{2+} or Fe^{2+}(h.s.) in eight-coordination] in the calcium ferrite structure; (2) that magnetite has Fe^{2+}(l.s.) in six-coordination and Fe^{2+}(h.s.) in eight-coordination in the calcium ferrite structure; and (3) that hematite has the same (corundum) structure but Fe^{3+}(l.s.). They conclude that $MgFeSiO_4$ in the calcium ferrite structure with Fe^{3+}(l.s.) is produced by pressures greater than 650 kbar. Fe_2SiO_4 first goes into a strontium plumbate structure (high-spin) and then into a calcium ferrite (half high-spin, half low-spin) at about 900 kbar. Apparently it is easier to spin-pair Fe^{3+} than Fe^{2+}, since the Fe^{2+} in the magnetite intermediate pressure phase is still high-spin.

SPIN-STATE Fe^{2+} IN LOWER MANTLE

The shock wave data discussed earlier offer good evidence that transitions to Fe^{2+}(l.s.) compounds are likely in the lower mantle. Under shock conditions such transitions occur below 650 kbar in hortonolite dunite and possibly in other iron compounds as well. Such a pressure will be achieved in the earth at 1550 km. However, phase transitions in shock experiments are often sluggish, so that these must be considered upper limits on the pressures at which such reactions can occur under hydrostatic conditions in geologic time.

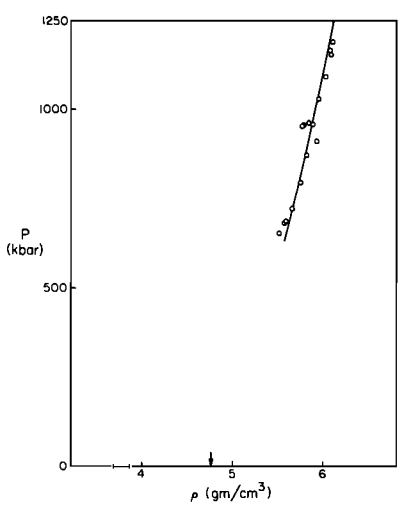

Fig. 3*a*. Predicted Hugoniot of hortonolite dunite assuming high-pressure phase is MgFe (l.s.) SiO_4 in a calcium ferrite structure with the properties given in Table 1: circles represent experimental data [*McQueen et al.*, 1967]; bar on lower scale shows initial density; arrow shows zero pressure density of high-pressure phase.

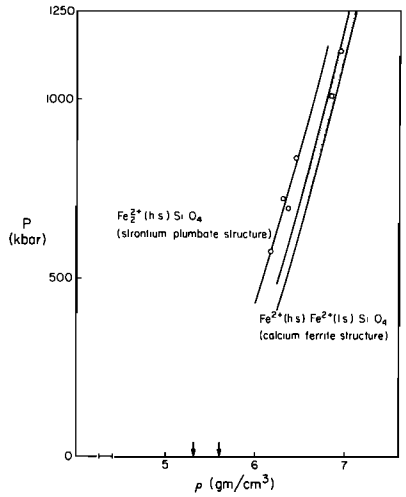

Fig. 3*b*. Predicted Hugoniots of Rockport fayalite assuming two possible high-pressure phases: strontium plumbate structure with high-spin iron having the density and elastic properties of wustite plus stishovite, and calcium ferrite structure. Symbols are as in Figure 3(*a*).

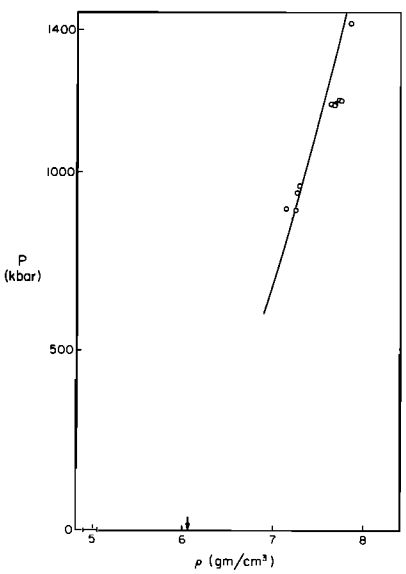

Fig. 3*c*. Hugoniot of hematite assuming that high-pressure phase has the density appropriate for low-spin Fe^{3+} in a corundum structure. The bulk modulus of the high-pressure phase has been chosen so as to fit the data of *McQueen et al.* [1967]. Symbols as in Figure 3(*a*).

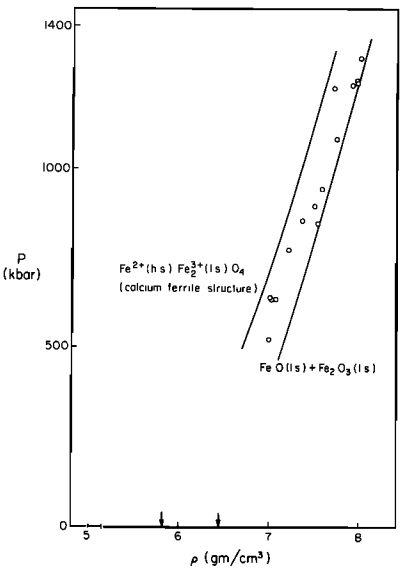

Fig. 3*d*. Predicted Hugoniots for magnetite assuming that the high-pressure phase is either a calcium ferrite structure (with high-spin Fe^{2+} and low-spin Fe^{3+}) or a mixture of the low-spin oxides. Symbol as in Figure 3(*a*).

In paper 1 the variation of the crystal field parameter with compression was discussed. The crystal field was separated into a part proportional to r^{-3} and a part proportional to r^{-5}, where r is the interatomic distance between the transition metal and the coordinated ion. This technique worked fairly well in predicting the zero-pressure spectra of several ferrous iron compounds. It has recently been shown that this point charge model predicts accurately the behavior of the spectrum of ruby with up to 15% volume compression [*Gaffney and Ahrens*, 1973]. We use this model below and expect the results to be accurate to about 10–20%.

The problem of crystal field effects is more complicated if we wish to consider the possibility of spin-pairing. The energy difference between states of different spin multiplicity will depend not only on the crystal fields but also on the magnitude of the electron repulsion energy. This energy enters into the calculation by way of the Racah parameters B and C [*Tanabe and Sugano*, 1956].

In an octahedral site the crystal field energy required to induce spin-pairing in Fe^{2+} will be about $(5B + 8C)/2$ [*Griffith*, 1966]. As the interatomic distance decreases, covalent

bonding is expected to lower B and C. Indeed, the value of B and C in Fe^{2+} in minerals (Gaffney, C. D. Cowan, and G. R. Rossman, in preparation, 1973) is less than that of the free ion. However, there is no simple relation between B, C, and r.

The variation of B and C with compression has been determined experimentally for a variety of transition metal ions and ligands (unfortunately, not for Fe^{2+}-O^{2-}). For oxides values of B seem to vary with r as r^n, where n is between 3 and 6 [*Stephens and Drickamer*, 1961*a*, *b*]. Attempts to infer variation with r for Fe-O combinations in a variety of oxides and silicates at zero pressure [*Gaffney*, 1972] have not been successful because of the strong effect of coordination. In the models below we will use both r^3 and r^6 as the variability of B and C with r.

Calculations of crystal field strengths combined with knowledge of the Racah parameters provide another means of bounding the pressures required to produce spin-pairing. The pressure required to induce spin-pairing in the high-spin phases such as $(Mg, Fe)_2SiO_4$ spinel or $(Mg, Fe)SiO_3$ ilmenite will be an upper limit, since the spin-paired state could be achieved earlier in some phase peculiar to low-spin Fe^{2+} (such as $MgFeSiO_4$ in the calcium ferrite structure). The upper limits are more than 1 Mbar for $(Mg, Fe)_2SiO_4$ (strontium plumbate structure) and $(Mg, Fe)SiO_3$ (ilmenite). However, for wustite, on the basis of elastic data of *Mizutani et al.* [1972] and dK/dP from Figure 2, transition pressures at 0°C will be 370 and 250 kbar for the lower and upper limits on the variability of B and C. At the higher temperatures of a geotherm, spin pairing is predicted at 460 and 340 kbar (1200 and 900 km). Although FeO is probably not a separate phase in the mantle, this will still be a good upper limit on the pressures of the high- to low-spin transition. As *Strens* [1969] pointed out, the local compressibility about Fe^{2+} in most oxides and silicates is probably much less variable than the bulk compressibility of the host. (It should be noted that this is not the same calculation as that undertaken by *Strens* [1969]. He attempted to estimate an equilibrium between FeO(l.s.) and FeO(h.s.). Furthermore, although he did use B and C lower than the free-ion values, he did not consider them to decrease more upon compression.) Static compression studies of FeO up to 300 kbar [*Clendenon and Drickamer*, 1966] indicate that the r^6 upper limit for variability of B and C is too high. No discontinuity in the lattice constant was seen up to 300 kbar, but the occurrence of spin pairing would probably produce one, because no change in structure (only in spacing) is required.

On the other hand, the lower limit of stability of Fe^{2+}(l.s.) in these low-spin phases will be a lower limit on the transition pressures. The low-spin compounds are predicted to be low-spin even at zero pressure. That is not to say that they are thermodynamically stable, but only that if they did exist at zero pressure they would be low-spin.

The result is that, with the present inaccuracies, primarily in predicting the Racah parameter, it is not possible to predict the exact pressure at which spin pairing can be expected in the lower mantle. Further experimental work, especially at low pressures on hortonolite and wustite, is required to resolve this difficulty. Nonetheless, we are assured that below 1200 km any Fe^{2+} in the earth's mantle will be spin-paired, and this reopens the question of the composition of the lower mantle.

Composition of the Lower Mantle

Given that Fe^{2+} will be in a low-spin state somewhere in the lower mantle, we turn to an investigation of its effects on geophysically observable quantities. The effect on the importance of radiative transfer was discussed earlier (paper 1), and the general results of that argument are still valid, i.e., radiative transfer will be important if Fe^{2+} is spin-paired but will be inhibited by crystal field absorption if it is not spin-paired.

Using the elastic properties given earlier (Table 1), the density ρ and the seismic parameter Φ can be calculated for various minerals and rocks in the mantle. A Murnaghan equation rather than a Birch-Murnaghan equation is used to extrapolate to high pressures, because it is probably more appropriate for the small dK/dP that have been adopted. The calculations were carried out using the continental geotherm of *Stacy* [1969] with $dK/dT = -1.5$ kbar/deg and $\alpha = 25 \times 10^{-6}$. An initial set of calculations was done using Ring-

wood's pyrolite composition with high-pressure transitions (*a*) through (*e*) occurring at a variety of levels. The range of the calculated $\Phi(=K/\rho)$ and ρ's is shown in Figure 4. Values deduced from seismic data by *Jordan and Anderson* [1973] are shown for comparison. The densities are much too low throughout the lower mantle, although the Φ's are acceptable. Agreement is best above 800 km, where a pyrolite composition is barely possible. This is not surprising, since pyrolite composition was, in fact, designed on the basis of upper mantle data. In the region above 800 km, the best pyrolite model has Fe^{2+} spin-paired in $MgFeSiO_4$ (calcium ferrite structure). No fit of pyrolite to the data can be obtained with high-spin iron. Below 800 km, no phase assemblage with a pyrolite composition fits the data.

Plotting the probable major mineral data and the observed seismic data in a ρ-Φ plot for various pressures on a geotherm, one can estimate the mineralogic composition of the lower mantle and then check the estimate as with the pyrolite model. Considering only Mg, Fe, and Si in $MgSiO_3$ (ilmenite or perovskite structure), (Mg, Fe)SiO_3 (ilmenite), Mg_2SiO_4 (strontium plumbate or potassium nickel fluoride structure), (Mg, Fe)$_2SiO_4$ (strontium plumbate), menite), the seismic results can be fit very well, as Figure 5 shows. The best fit is obtained with a composition $Mg_{1.67}Fe_{0.33}SiO_4$ at 650 km varying fairly smoothly to about $MgFeSiO_4$ (calcium ferrite), and $FeSiO_3$ (il-$Mg_{0.89}Fe_{0.33}SiO_{3.21}$ at the core-mantle boundary. The latter value corresponds to 0.40MgO + 0.15FeO + 0.45SiO_2 (mole fraction), which can be compared to 0.38MgO + 0.16FeO + 0.46SiO_2 (mole fraction) determined by *Anderson* [1970] to be the average composition of the lower mantle. All the iron in this model is spin-paired below 630 km. Above about 1500 km the low-spin ferrous mineral will be $MgFeSiO_4$, but $FeSiO_3$ is present at greater depths. The values for ρ_0 and Φ_0 in Table 1 range from 3.97 to 4.28 g/cm^3 and 56.0 to 67.8 (km/sec)^2, respectively, for the lower mantle mineral assemblages at $P = 0$, $T = 1600°C$, which is the approximate value of the lower mantle adiabat extrapolated to the surface [*Clark and Ringwood*, 1964]. This can be compared with the values of 4.11–4.14 g/cm^3 and 55.0–56.5 (km/sec)^2 determined from seismic data [*Anderson and Jordan*, 1970] to be the appropriate average values for the lower mantle.

A brief comment is in order about the possibility of other elements, primarily Al, Ca, and Na, in the lower mantle. The effect of the addi-

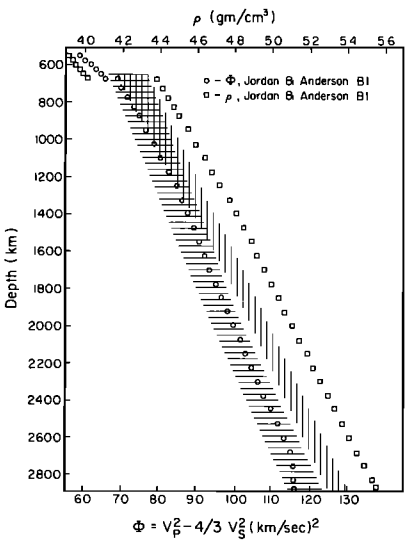

Fig. 4. Range of values calculated for density (vertical pattern) and seismic parameter (horizontal pattern) with a pyrolite bulk composition. Observed values are from *Jordan and Anderson* [1973].

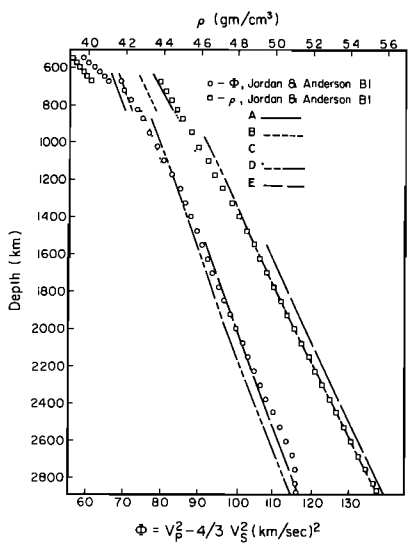

Fig. 5. Density and seismic parameter for several possible mantle assemblages (see Table 2).

tion of the oxides or silicates of these metals can be inferred from Table 1. All three minerals will lower the density, although for Al_2O_3 the effect will be small. The seismic parameters will be lowered by addition of Al_2O_3 and to a lesser extent by $NaAlSiO_4$ but will be raised by addition of $CaSiO_3$. Since the fit to the density of the lower mantle is quite good but the calculated Φ is somewhat too high, additions of up to about 10% Al_2O_3 might be possible without jeopardizing the fit to the observations. Only small amounts of $NaAlSiO_4$ and $CaSiO_3$ can be accommodated, however, because of their large effect on density.

ORIGIN OF THE UPPER MANTLE

The likelihood of iron and silicon enrichment in the lower mantle relative to the upper mantle has been shown. The presence of a separate phase containing Fe^{2+} makes it possible for the lower mantle to retain iron. At low pressures in silicate systems, it is usually found that silica and iron are concentrated in the early-melting components, and so they might be removed by any type of partial melting. However, at several hundred kilobars Si should be six-coordinated and Fe^{2+} should be spin-paired, so that there is no reason to expect behavior similar to that at low pressures. Indeed, by extension of the argument of *Burns and Fyfe* [1964] and *Curtis* [1964], Fe^{2+} should prefer the solid to the liquid if spin-paired. This effect should be accentuated by the small ionic radius of Fe^{2+}(l.s), and so it can be expected that if the lower mantle were ever partially molten it should be enriched in iron relat've to, say, the upper mantle, which would receive the early melt. If the Fe^{2+} solid being left behind in the lower mantle were $FeSiO_3$, some silica enrichment would also occur. It seems, therefore, that the upper mantle may be a differentiate of the whole mantle, just as basalt is commonly regarded as a differentiate of the upper mantle (pyrolite). It is also possible, of course, that iron enrichment of the lower mantle is an original property of the earth.

The upper mantle, for which pyrolite can be taken as a good approximation, contains much less FeO and SiO_2 than is inferred here for the lower mantle. *Ringwood* [1966] assumes that the whole mantle is uniform in composition (pyrolite) and deficient in SiO_2 and FeO compared to carbonaceous chondrites, the presumed parent material for the earth and the other terrestrial planets. He therefore devised a scheme by which ferromagnesian silicates were reduced in the high-temperature terminal stages of accretion and the reduced Fe and Si entered the core, thereby depleting the mantle in FeO and SiO_2. The present composition of the mantle can be matched by chondrite abundances [*Anderson et al.*, 1971], and thus the need for the mantle material to be exposed to the reduction processes envisaged by *Ringwood* [1966] is removed, as is the main argument that silicon is the light alloying element in the core.

Acknowledgments. This study was supported by the National Science Foundation under grants GA 21396 and GA 12703. The authors thank G. F. Davies for permission to use the results of unpublished calculations; they have also benefited from discussions with W. B. Kamb. Roger Burns provided a useful critical review.

REFERENCES

Abu-Eid, R. M., R. G. Burns, and H. K. Mao, A blue high pressure phase for gillespite, *Eos Trans. AGU* (abstract), *54*, 498, 1973.

Anderson, D. L., Chemical inhomogeneity of the mantle, *Earth Planet. Sci. Lett.*, *5*, 89–94, 1968.

Anderson, D. L., Bulk modulus-density systematics, *J. Geophys. Res.*, *74*, 3857–3864, 1969.

Anderson, D. L., Petrology of the mantle, *Mineral. Soc. Amer. Spec. Pap.*, *3*, 85–93, 1970.

Anderson, D. L., and O. L. Anderson, The bulk modulus-volume relationship for oxides, *J. Geophys. Res.*, *75*, 3494–3500, 1970.

Anderson, D. L., and T. Jordan, The composition of the lower mantle, *Phys. Earth Planet. Interiors*, *3*, 23–35, 1970.

Anderson, D. L., C. Sammis, and T. Jordan, Composition and evolution of the mantle and core, *Science*, *171*, 1103–1112, 1971.

Anderson, O. L., E. Schreiber, R. L. Lieberman, and N. Soga, Elastic constant data on minerals, *Rev. Geophys. Space Phys.*, *6*, 491–524, 1968.

Burns, R. G., *Mineralogical Applications of Crystal Field Theory*, 224 pp., Cambridge University Press, London, 1970.

Burns, R. G., and W. S. Fyfe, Site preference energy and selective uptakes of transition metal ions from a magma, *Science*, *144*, 1001–1003, 1964.

Clark, S. P., Jr., Radiative transfer in the earth's mantle, *Eos Trans. AGU*, *38*, 931–938, 1957.

Clark, S. P., Jr., and A. E. Ringwood, Density distribution and constitution in the mantle, *Rev. Geophys. Space Phys.*, *2*, 35–88, 1964.

Clendenon, R. L., and H. G. Drickamer, Lattice parameters of nine oxides and sulfides as a function of pressure, *J. Chem. Phys., 44,* 4223–4228, 1966.

Curtis, C. D., Applications of the crystal-field theory to the inclusion of trace elements in minerals during magmatic differentiation, *Geochim. Cosmochim. Acta, 28,* 389–403, 1964.

Davies, G. F., and D. L. Anderson, Revised shock-wave equations of state for high-pressure phases of rocks and minerals, *J. Geophys. Res., 76,* 2617–2627, 1971.

Gaffney, E. S., Crystal field effects in mantle minerals, *Phys. Earth. Planet. Interiors, 6,* 385–390, 1972.

Gaffney, E. S., and T. J. Ahrens, Optical absorption spectra of ruby and periclase at high shock pressures, submitted to *J. Geophys. Res.,* 1973.

Griffith, J. S., *The Theory of Transition-Metal Ions,* p. 238, Cambridge University Press, London, 1966.

Johnson, L. R., Array measurements of P velocities in the lower mantle, *Bull. Seismol. Soc. Amer., 59,* 973–1008, 1969.

Jordan, T., and D. L. Anderson, Earth structure from free oscillations and travel times, submitted to *Geophys. J. Roy. Astron. Soc.,* 1973.

McQueen, R. G., S. P. Marsh, and J. N. Fritz, Hugoniot equations of state of twelve rocks, *J. Geophys. Res., 72,* 4999–5036, 1967.

Mizutani, H., Y. Hamano, S. Akimoto, and O. Nishizawa, Elasticity of stishovite and wustite (abstract), *Eos Trans. AGU, 53,* 527, 1972.

Novak, G. A., and G. V. Gibbs, The crystal chemistry of the silicate garnets, *Amer. Mineral., 56,* 791–825, 1971.

Ringwood, A. E., The chemical composition and origin of the earth, in *Advances in Earth Science,* edited by P. Hurley, p. 287–356, MIT Press, Boston, 1966.

Ringwood, A. E., Phase transformations and the constitution of the mantle, *Phys. Earth Planet. Interiors, 3,* 109–155, 1970.

Shannon, R. D., and C. T. Prewitt, Effective ionic radii in oxides and fluorides, *Acta Crystallogr., Sect. B, 25,* 925–946, 1969.

Stacy, *Physics of the Earth,* p. 259, John Wiley, New York, 1969.

Stephens, D. R., and H. G. Drickamer, *J. Chem. Phys., 35,* 424–426, 1961*a*.

Stephens, D. R., and H. G. Drickamer, *J. Chem. Phys., 35,* 427–429, 1961*b*.

Strens, R. G. J., Pressure-induced spin-pairing in gillespite, $BaFeSi_4O_{10}$, *Chem. Commun., 777,* 1966.

Strens, R. G. J., The nature and geophysical importance of spin-pairing in minerals of iron (II), in *The Application of Modern Physics to the Earth and Planetary Interiors,* edited by S. K. Runcorn, pp. 213–220, Academic, New York, 1969.

Tanabe, Y., and S. Sugano, On the absorption spectra of complex ions, 3, The calculation of the crystalline field strength, *Int. J. Phys. Soc. Jap., 9,* 864–877, 1956.

Whitcomb, J. H., and D. L. Anderson, Reflection of *P'P'* seismic waves from discontinuities in the mantle, *J. Geophys. Res., 75,* 5713–5728, 1970.

(Received November 15, 1972;
revised May 1, 1973.)